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FT-IR and FT-Raman study of hydrogen bonding in *p*-alkylcalix[8]arenes

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ABSTRACT

The FTIR and FT Raman spectra of *p*-alkylcalix[8]arenes (alkyl = *tert*-butyl, isononyl) were recorded. Analysis of IR spectra showed that the cyclic cooperative intramolecular hydrogen bond is realized in calix[8]arene. It was found that the strength of the cyclic cooperative intramolecular hydrogen bond in the series of alkyl derivatives of calix[8]arenes depends very little on the replacement of the *p*-*tert*-butyl groups by the more bulky isononyl group. From our data follows that the orientation of aromatic fragments in calixarene molecules depends on the type of alkyl substituent.

An analysis of the changes in the IR spectra with heating and dissolution shows that the conformation of the "pleated-loop" is retained in *p*-*tert*-butylcalix[8]arene. It turned out that the intramolecular hydrogen bond is a "probe" of the conformation of calixarene molecules and IR spectroscopy is a unique method that allows one to follow the slightest nuances of changes in the H-bound system of these supermolecules.

1. Introduction

The increased interest in the study of calixarenes and their physico-chemical properties is explained not only by the purely scientific interest of researchers in the field of chemistry to unusual complex structures and the rich conformational possibilities of their molecules, but also by the potential for widespread practical application of this class of compounds [1–7]. Calixarenes are macrocycles containing hydroxyl groups involved in the formation of intramolecular hydrogen bonds. These compounds are able to effectively bind neutral molecules, ions and are used in ecology, medicine and nuclear power engineering [1–7]. It has been shown that *para*-*tert*-butylcalixarenes are able to extract cesium from alkaline solutions [8,9]. A characteristic feature of these compounds is their low solubility in organic solvents used in the extraction process. Therefore isononyl derivatives of calix[8]arene, which are better soluble in organic solvents and allow to extract Cs, Am, and Tc from alkaline solutions have been prepared [10]. It turned out that *n*-isononylcalix[8]arene extracts cesium and americium in a much less effectively than the *tert*-butyl analogue due to the varying degree of aggregation in the organic phase [10]. Isononyl derivative exists in monomeric form and *tert*-butylcalix[8]arene forms aggregates [10]. To obtain a soluble and effective cesium and americium extractant, *n*-alkylcalix[8]arenes with various ratios of *tert*-butyl and isononyl groups on the upper rim of the calixarene platform were synthesized. Therefore, the study of the structure and hydrogen bonding in calixarenes is one of the most important problems of physical chemistry. IR spectroscopy is the traditional method for studying hydrogen bonds and the conformation of calixarens [11–24]. However, the possibilities of vibrational spectroscopy for this class of compounds are not widely used, many authors are limited to study the frequency of the stretching vibrations of hydroxyl groups [11]. In recent years, articles have been published in which a fairly detailed analysis of the hydrogen bonding system for a number calixarenes has been carried out [13]. Raman spectroscopy studies of calixarenes are very limited [13]. Quantum chemical calculations were carried out for modeling the hydrated sodium and potassium ions transport through an calixarene derivative [25].

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